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The CN_7^- Anion

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Abstract: Several salts containing the CN_7^- anion were prepared by deprotonation of 5-azido-1*H*-tetrazole (**1**). The highly explosive compounds hydrazinium (**2**), ammonium (**3**), aminoguanidinium (**4**), guanidinium (**5**), lithium (**6**), sodium (**7**), potassium (**8**), cesium (**9**), and calcium (**10**) azidotetrazolate were characterized by low temperature single X-ray diffraction. Other analytic methods, such as IR and Raman spectroscopy, multinuclear NMR spectroscopy, mass spectrometry, and differential scanning calorimetry were performed when possible since some of the metal salts explode spontaneously. **2** contains the highest nitrogen content (87.48%) of all known tetrazole salts. The impact, friction, and electrical spark sensitivity of **2**, **3**, **4**, and **5** were measured, resulting in values which belong to primary explosives. In addition, the heats of formation of **2**, **3**, and **4** were calculated using the CBS-4M level of quantum mechanical theory. These, in turn, were used to estimate detonation pressure $p_{\text{C-J}}$ and velocity D_{det} as well as the specific impulse I_{sp}.

Introduction

Many scientists are attracted to nitrogen-rich compounds, since their tendencies toward instability pose considerable technical challenges in their synthesis and isolation. N-rich molecules are considered as prime candidates for "green" energetic materials[1] since the materials exhibit desirable performance characteristics in high explosives (HEs) or in propellant formulations, but the main combustion products are molecular nitrogen. Numbered among the compounds (including hydrazoic acid,[2] tetraazidomethane,[3] hydrazinium[4,5] and ammonium azide,[6] and salts containing the N_5^+ cation;[7] see Figure 1) that have the highest nitrogen content are many tetrazole derivatives.[8] 5-N substituted tetrazoles, e.g., 5-aminotetrazole,[9] 5,5′-azotetrazolates,[10] bis(1*H*-tetrazolyl)amine (H_2BTA),[11] and 5,5′-bis(1*H*-tetrazolyl)hydrazine (BTH)[12] show nitrogen contents above 82%. Tetrazoles often have the outstanding benefit of combining a high nitrogen content (yielding highly endothermic compounds) with good thermal stabilities, due to their aromatic ring system. The tetrazole with the highest N-content is 5-azido-1*H*-tetrazole (**1**), which was first described in patents in 1939[13] and was also recently reinvestigated in our research group.[14] Salts of the highly explosive **1** are rarely described in the literature.[15,16] The reason for this may be the extreme sensitivities. Only the IR data of the ammonium and silver 5-azidotetrazolate can be found in the literature.[15,16] Although 5-azidotetrazolates are probably too sensitive for any applications, they are still interesting compounds since they contain a binary CN_x^- ($x = 7$) anion.

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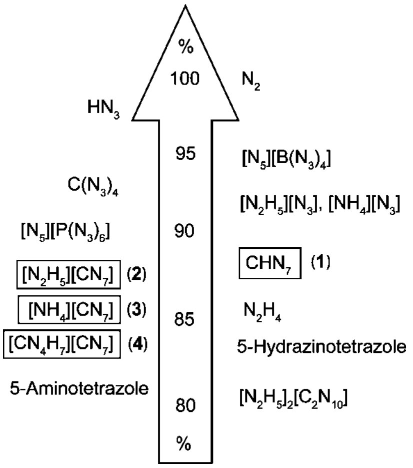

Figure 1. Selected examples of molecules containing a nitrogen content of more than 80%.

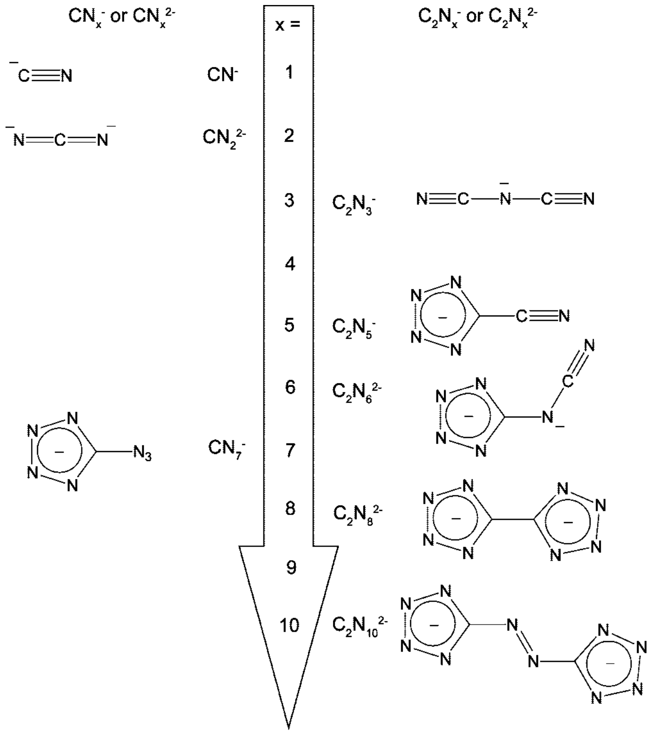

Figure 2. Selected N-rich C−N anions.

The most prominent binary carbon−nitrogen anion is the cyanide anion (CN^-). Salts of hydrogen cyanide are among the most important chemicals used in industrial, pharmaceutical, and agricultural processes.[17] Despite the prevalence of the cyanide anion, there are only a few examples of other known binary CN anions. There are different ways to systematically divide binary CN anions, such as the charge [singly charged ions, e.g., dicyanamide ($NC-N-CN^-$);[18] doubly charged ions, e.g., cyanamide (NCN^{2-});[19] and triply charged ions, e.g., tricyanomelaminate ($(NC-NCN)_3]^{3-}$ [20] or the carbon−nitrogen ratio. Using the carbon−nitrogen ratio as a criterion, CN anions may be grouped into three classes: (i) nitrogen-rich (C_xN_y, $x < y$), e.g., cyanamide and dicyanamide; (ii) carbon-rich CN anions (C_xN_y, $x > y$), e.g., tricyanomethanide ($C(CN)_3^-$);[21] or (iii) CN anions with an equal number of carbon and nitrogen atoms (C_xN_y, $x = y$), e.g., cyanide. Most of the nitrogen-rich CN anions are based on the tetrazole ring such as cyanotetrazolate ($C_2N_5^-$),[22] 5-cyaniminotetrazolinediide $C_2N_6^{2-}$,[23] 5,5′-bis(tetrazolate) ($C_2N_8^{2-}$),[24] 5,5′-azotetrazolate ($C_2N_{10}^{2-}$),[25] 3,6-bis(2*H*-tetrazol-5-yl)-1,2,4,5-tetrazinediide, ($C_4N_{12}^{2-}$),[26] and 5-azidotetrazolate CN_7^-.[15] The nitrogen-rich anions are of special interest, as they represent salts with high nitrogen contents, having high positive heats of formation and often showing remarkable thermodynamic and kinetic stabilities.[27] A compendium of selected $C_xN_y^{z-}$ (x = max. 2, $y = 1-10$, $z = 1-2$) anions is depicted in Figure 2.

The CN_7^- anion represents a milestone in the development of nitrogen-rich "green" energetic materials. Energetic materials are most commonly used either in high explosives (HEs) or in propellant formulations. Whereas the performance of HEs can be related to heat of detonation (Q), detonation pressure ($p_{C\text{-}J}$), and detonation velocity (D_{det}), the performance of rocket/missile propellants is best characterized by their density and specific impulse (I_{sp}).[28] Equally important, an increase of the I_{sp} of only 20 s would be expected to increase the payload by ca. 100%. Moreover, for gun propellants, erosivity is an additional concern and lower reaction temperatures and a high N_2/CO ratio of the reaction gases are desirable.[29] Recent modeling and testing have shown that the presence of high concentrations of nitrogen species in the combustion products of propellants can reduce gun barrel erosion by promoting the formation of iron nitride rather than iron carbide on the interior surface of the barrel.

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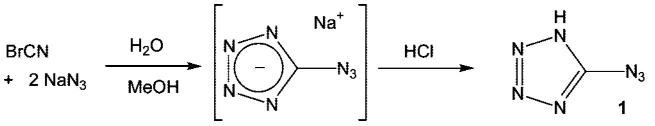
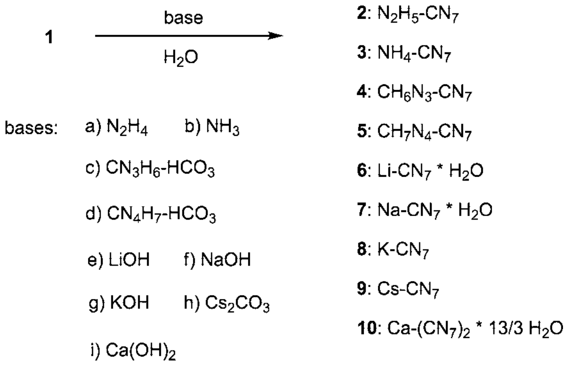
Scheme 1. Synthesis of 5-Azidotetrazole



Scheme 2. Syntheses of the Azidotetrazolate Salts **2**−**10**



Thus compounds such as hydrazinium azotetrazolate (N% = 85.19%) or triaminoguanidinium azotetrazolate (N% = 82.32%) show promise for use in low erosivity gun propellants. Both the U.S. Army and the U.S. Navy are pursuing new, high-nitrogen gun propellants.

Here we report on a series of highly energetic salts containing the CN_7^- anion, which were all characterized using X-ray diffraction. The further chemical characterization (e.g. IR, Raman, NMR, elemental analysis, DSC) is as extensive as possible, since several metal 5-azidotetrazolates, when completely dried, explode spontaneously without any handling even in the dark. While these metal salts are extremely explosive and probably only of academic interest, the nitrogen-rich salts (hydrazinium, ammonium, aminoguanidinium, and guanidinium) are stabilized via hydrogen bonds and represent promising energetic materials. In addition these salts show the highest N-content ever reported for tetrazolate salts.

Results and Discussion

Synthesis. The most facile and selective synthesis of 5-azido-1*H*-tetrazole (**1**) is the reaction of cyanogen bromide with 2 equiv of sodium azide in aqueous solution at low temperatures followed by an acidic workup using diluted hydrochloric acid. (Scheme 1).

Salts **2**−**10** were synthesized according to Scheme 2. Except for the synthesis of hydrazinium 5-azidotetrazolate (**2**) in THF, all reactions were carried out in water. Potassium and cesium 5-azidotetrazolate explode spontaneously when dry, while rubidium 5-azidotetrazolate even explodes spontaneously during the crystallization process in concentrated solution.

CAUTION: *5-Azido-1H-tetrazole as well as its salts* **2**−**10** *are extremely energetic compounds with increased sensitivities towards various stimuli. Therefore proper protective measures (safety glasses, face shield, leather coat, earthened equipment and shoes, Kevlar gloves and ear plugs) should be used all time during work on* **2**−**10**. *All compounds should be stored in explosive cases since they can explode spontaneously.*

2 was isolated by filtration after adding hydrazine in THF solution at room temperature to **1** (also dissolved in THF). Single crystals could be obtained from recrystallization from a MeOH/THF mixture. The ammonium salt **3** was obtained by treating **1** with a slight excess of aqueous ammonia solution. After the solution was evaporated, the colorless crude product was recrystallized from ethanol. Aminoguanidinium and guanidinium 5-azidotetrazole were synthesized by the reactions of **1** with aminoguanidinium bicarbonate and guanidinium bicarbonate, respectively. Both compounds were recrystallized from wet methanol. Lithium, sodium, and potassium 5-azidotetrazolate were obtained by simple evaporation of aqueous solutions containing **1** and 1 equiv of the corresponding metal hydroxide. **6** and **7** are “relatively” stable towards external stimuli, while even small amounts of potassium 5-azidotetrazolate explode violently. The cesium salt was synthesized by treating **1** with 0.5 equiv of cesium carbonate. The aqueous solution was left for crystallization on a watch glass, and “fortunately” three single crystals could be isolated from the border of the solution. A few hours later the whole preparation exploded spontaneously. Also the synthesis of rubidium 5-azidotetrazolate has been tried a few times. However, we never could observe any solid material, and the reaction mixture (left undisturbed in an explosive case and in the dark) detonated spontaneously for each preparation. The calcium salt **10** could be prepared without any problems by the reaction of an aqueous suspension of $Ca(OH)_2$ with **1**. After filtration, single crystals were obtained from this solution by simple standing in air at room temperature.

Molecular Structures. The single crystal X-ray diffraction data were collected using an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector. The data collection was undertaken using the CRYSALIS CCD software,[30] and the data reduction was performed with the CYRSALIS RED software.[31] The structures were solved with SIR-92[32] and refined with SHELXL-97[33] implemented in the program package WinGX[34] and finally checked using PLATON.[35] Due to the chiral space group of the structure of **2** Friedel pairs were merged. In all structures potential hydrogen atoms have been observed and freely refined. Selected data and parameters from the X-ray data collection and refinement are given in Tables 1 and 2. Further information regarding the crystal-structure determination have been deposited with the Cambridge Crystallographic Data Centre[36] as supplementary publication Nos. 677382, (**2**), 675485 (**3**), 699844 (**4**), 699848 (**5**), 699845 (**6**), 675486 (**7**), 699847 (**8**), 699846 (**9**), and 699849 (**10**).

Hydrazinium 5-azidotetrazolate (**2**) crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell and a density of 1.568 g cm^{-3}. The molecular moiety is shown in Figure 3. In general, in all structures presented in this work the CN_7 anions have nearly identical geometries. The N−N and C−N bond lengths within the tetrazole ring are all between

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(30) *CrysAlis CCD*, Oxford Diffraction Ltd., Version 1.171.27p5 beta (release 01-04-2005 CrysAlis171.NET).

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(36) Crystallographic data for the structure(s) have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: int.code_(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit-@ccdc.cam.ac.uk).

Table 1. Crystallographic Data of **2**−**6**

	2	**3**	**4**	**5**	**6**
formula	CH_5N_9	CH_4N_8	$C_2H_7N_{11}$	$C_4H_{14}N_{20}O$	CH_2N_7OLi
FW [g mol^{-1}]	143.14	128.12	185.19	358.35	135.03
crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1$	P-1	$P2_1/c$	$P2_1/c$
color/habit	colorless needles	colorless needles	colorless blocks	colorless rods	colorless needles
size, [mm]	0.07 × 0.07 × 0.21	0.01 × 0.05 × 0.08	0.03 × 0.07 × 0.18	0.03 × 0.05 × 0.06	0.05 × 0.06 × 0.17
a [Å]	10.8114(5)	3.9103(3)	9.7652(8)	9.5374(8)	8.9207(5)
b [Å]	7.4641(4)	6.9140(4)	9.7803(9)	15.3120(9)	4.6663(2)
c [Å]	7.6676(4)	9.9127(6)	10.0434(9)	10.5731(6)	12.8648(6)
α [deg]	90	90	71.327(8)	90	90
β [deg]	101.437(5)	99.177(6)	74.399(7)	94.361(7)	95.608(5)
γ [deg]	90	90	63.962(9)	90	90
V [Å^3]	606.47(5)	264.57(3)	807.2(1)	1539.6(2)	532.96(5)
Z	4	2	4	4	4
ρ_{calcd} [g cm^{-3}]	1.568	1.608	1.524	1.546	1.683
μ [mm^{-1}]	0.126	0.129	0.120	0.125	0.139
F(000)	296	132	384	744	272
$\lambda_{MoK\alpha}$ [Å]	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
T [K]	100	200	200	100	200
θ min−max [deg]	3.8, 26.0	4.2, 27.1	3.9, 26.0	3.8, 25.5	4.1, 26.5
dataset	−12:13; −9:8; −9:8	−4:5; −8:8; −12:12	−11:12; −12:11; −12:12	−11:11; −18:16; −12:6	−10:11; −5:5; −14:16
reflections collected	3021	2806	4173	7183	2650
independent reflections	1192	623	3118	2835	1096
R_{int}	0.025	0.059	0.027	0.082	0.029
observed reflections	824	383	1552	1128	785
no. parameters	111	98	291	282	99
R_1 (obsd)	0.0305	0.0307	0.0450	0.0490	0.0313
wR_2 (all data)	0.0767	0.0637	0.1154	0.1288	0.0869
S	0.93	0.91	0.93	0.88	1.05
resd. dens. [e Å^{-3}]	−0.24, 0.19	−0.16, 0.22	−0.22, 0.21	−0.23, 0.27	−0.19, 0.19
device type	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
solution	SIR-92	SIR-92	SIR-92	SIR-92	SIR-92
refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
absorption correction	multiscan	multiscan	multiscan	multiscan	multiscan
CCDC	677 382	675 485	699 844	699 848	699 845

typical single and double bond lenghts[37] and are listed in Tables S1−S4 in the Supporting Information. The geometry of the azidotetrazolate anions is similar to that observed for neutral 5-azido-1*H*-tetrazole (**1**). In the structures of **2**−**10**, the N1−N2 and the N5−N6 bond lengths are shorter than the neutral counterparts, while the N2−N3 as well as the C1−N5 distances are found to be longer. For the N3−N4, N1−C1, N4−C1, and N6−N7 bond distances, no similar trend is observed. The constitution of the azide group is similar to those of other covalent carbon bonded azide groups, e.g., azidoformamidinium salts.[38,39] The azide group is bent (N5−N6−N7 = 171.5(3)°), which is quite common for covalent azides and can be explained by hyperconjugation effects.[40] Also the outer $N_\beta-N_\gamma$ distance is significantly shorter (in the range of a N−N triple bond) than the inner one. In the structure of **2**, the hydrazine bond length of N8−N9 = 1.452(2) Å is also found in hydrazinium chloride (1.45 Å)[41] or hydrazinium 5,5′-azotetrazolate.[8]

Although **2** has the highest nitrogen content observed in this work, its sensitivities are lower in comparison to those of the water free alkaline metal salts. This may be due to the strong hydrogen bond network, which can be found in the packing of **2** (Figure 4) along the $b-c$ plane. The single layers are connected by a weak hydrogen bond involving the outer azide nitrogen atom N7 (N9−H9A···N7 = 0.89(2), 2.60(2), 3.335(2) Å, 140(1)°).

Ammonium 5-azidotetrazolate (**3**) crystallizes in the monoclinic chiral space group $P2_1$ with two molecules in the unit cell and a density of 1.608 g cm^{-3}. A view of the coordination of the ammonia cations is illustrated in Figure 5. The packing is strongly influenced by the four different hydrogen bonds. Also the nitrogen atom N7 of the azide group participates as a weak hydrogen bond acceptor. The extensive hydrogen-bonding network is better explained in the formalism of a graph set analysis.[42] Particularly the motifs $C_2^2(6)$ and $R_2^2(5)$ can be found. This combination of chains and rings yields bands in the packing of **3** (Figure 6). The connection between the rings is formed by an additional hydrogen bridge.

1-Aminoguanidinium 5-azidotetrazolate (**4**) crystallizes in the triclinic space group $P\bar{1}$. The density 1.524 g cm^{-3} is lower in

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Table 2. Crystallographic Data of **7**−**10**

	7	8	9	10
formula	CN_7Na*H_2O	CN_7K	CN_7Cs	$C_6H_{32}Ca_3N_{42}O_{16}$
FW [g mol^{-1}]	151.09	149.18	242.99	1068.98
crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_12_12_1$	$C2/c$
color/habit	colorless needles	colorless rods	colorless plates	colorless needles
size, [mm]	0.04 × 0.05 × 0.09	0.03 × 0.07 × 0.14	0.05 × 0.06 × 0.07	0.05 × 0.06 × 0.09
a [Å]	11.203(2)	9.7759(9)	4.3082(1)	24.448(5)
b [Å]	7.138(2)	6.2990(6)	7.1345(2)	6.616(5)
c [Å]	14.409(2)	8.4533(6)	18.6869(9)	28.057(5)
α [deg]	90	90	90	90
β [deg]	91.630(1)	96.720(8)	90	109.246(5)
γ [deg]	90	90	90	90
V [Å^3]	1151.8(4)	516.96(8)	574.38(3)	4285(3)
Z	8	4	4	4
ρ_{calcd} [g cm^{-3}]	1.743	1.917	2.810	1.657
μ [mm^{-1}]	0.207	0.927	6.357	0.495
F(000)	608	296	440	2200
$\lambda_{MoK\alpha}$ [Å]	0.710 73	0.710 73	0.710 73	0.710 73
T [K]	200	100	100	100
θ min−max [deg]	4.0, 26.0	4.0, 25.5	4.3, 26.8	3.7, 25.5
dataset	−13:13; −8:8; −17:14	−11:9; −7:7; −10:10	−5:5; −8:9; −13:23	−23:29; −8:7; −3:28
reflections collected	5726	2090	3179	9922
independent reflections	2254	956	1227	3947
R_{int}	0.041	0.028	0.027	0.064
observed reflections	830	678	1074	2220
no. parameters	197	82	82	369
R_1 (obsd)	0.0313	0.0315	0.0227	0.0423
wR_2 (all data)	0.0798	0.0763	0.0398	0.0992
S	0.71	0.99	0.92	0.96
resd. dens. [e Å^{-3}]	−0.22, 0.39	−0.35, 0.60		−0.52, 0.46
device type	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
solution	SIR-92	SIR-92	SIR-92	SIR-92
refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
absorption correction	multiscan	multiscan	multiscan	multiscan
CCDC	675 486	699 847	699 846	699 849

comparison to those of **1**−**3**. The unit cell contains two different molecular moieties. In general the aminoguanidinium cations have geometries also found in aminoguanidinium chloride,[43] nitrate,[44] or perchlorate.[45] They are nearly planar (N10−C2−N8−N9 = 2.2(2)°, N20−N19−C4−N21 = −3.1(4)°), with C−N bond lengths between 1.31 and 1.33 Å observed. These distances are substantially shorter than C−N single bonds (1.47 Å) but

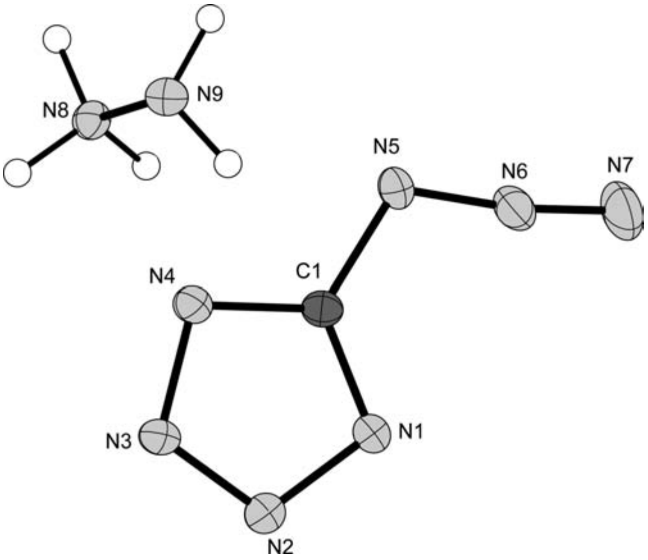

Figure 3. Molecular moiety of hydrazinium 5-azidotetrazolate. The ellipsoids represent the 50% probability level.

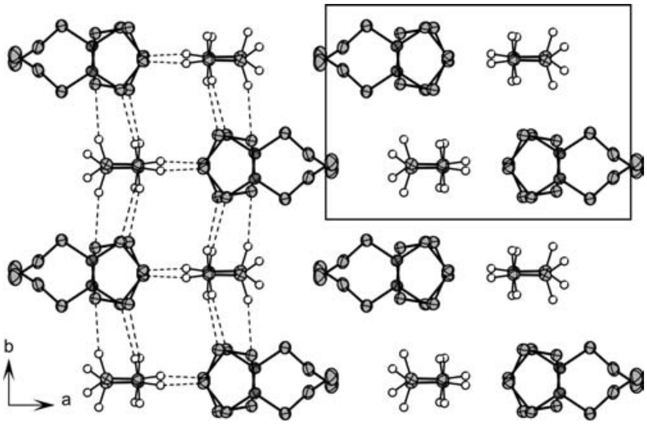

Figure 4. View on the packing of **2** along the *c* axes showing the hydrogen bonds. Selected hydrogen bonds within the layers: N8−H8C···N^{i} = 0.92(2), 2.01(2), 2.911(2) Å, 164(1)°; N9−H9B···N4^{ii} = 0.90(2), 2.24(2), 3.05(2) Å, 150(1)°; N8−H8A···N1^{iii} = 0.930(2), 2.035(2), 2.888(2) Å, 153 (2)°; N9−H9A···N5^{iv} = 0.89(2), 2.51(2), 3.128(2) Å, 127(1)°; (i) −*x*, −*y*, 1 − *z*; (ii) −*x*, 0.5 + *y*, 1.5 − *z*; (iii) −*x*, 1 − *y*, 1 − *z*; (iv) −*x*, −0.5 + *y*, 1.5 − *z*.

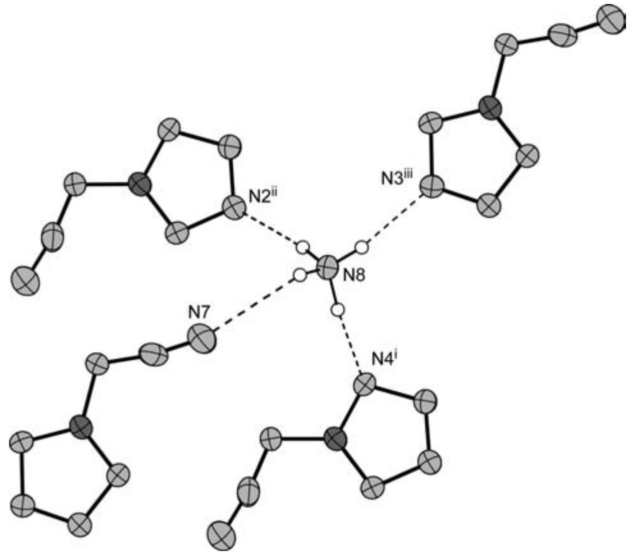

Figure 5. Hydrogen bonds in the packing of **3**. Selected hydrogen bonds (D−H···A, *d* D−H [Å], *d* H−A [Å], *d* D−A [Å], angle D−H···A [deg]): N8−H8B···N4^{i}, 1.05(5), 1.89(5), 2.933(4), 175(4); N8−H8C···N2^{ii}, 0.87(3), 2.05(3), 2.917(5), 171(3); N8−H8D···N3^{iii}, 0.88(4), 2.05(4), 2.923(4), 169(6); N8−H8A···N7, 0.92(4), 2.57(3), 3.116(4), 119(2); (i) 1 − *x*, −0.5 + *y*, 1 − *z*; (ii) 1 − *x*, 0.5 + *y*, 1 − *z*; (iii) 1 + *x*, *y*, −1 + *z*.

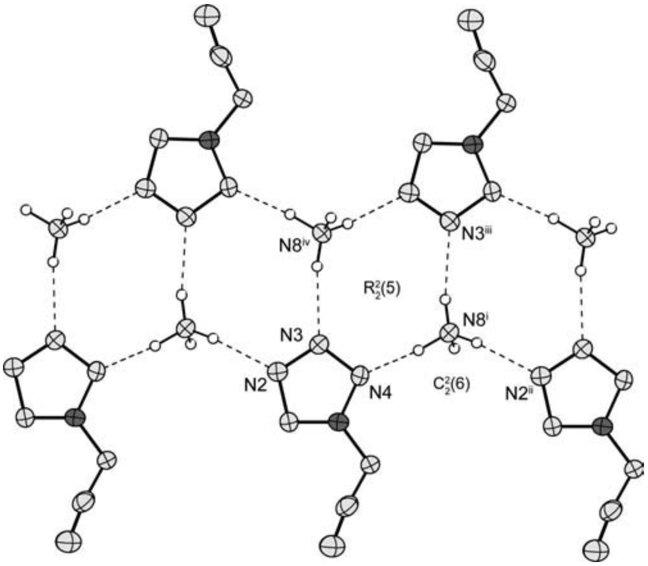

Figure 6. Graph sets of interest in the packing of **3**. Symmetry codes: (i) 1 − *x*, 0.5 + *y*, 1 − *z*; (ii) *x*, 1 + *y*, *z*; (iii) −*x*, 0.5 + *y*, 2 − *z*; (iv) −1 + *x*, *y*, *z*.

significantly longer than C═N double bonds (1.22 Å) and show explicitly the delocalization of the positive charge. The packing of **4** is characterized by the formation of layers, which are illustrated in Figure 7. The layers have distances of ca. 3.25 Å. Within the layers more than 10 different hydrogen bridges, which are smaller than the sum of the van der Waals radii of two nitrogen atoms ($r_{A(N)} + r_{D(N)} = 3.10$ Å),[46] are formed. In contrast to the structures of **2** and **3** also the nitrogen atom N5 of the azide group participates in a weak hydrogen bond (N10−H10A···N5 = 0.87(3), 2.42(3), 3.262(3) Å, 164(2)°). In addition to the graph sets shown in Figure 7, two chains ($C^2_2(9)$) are formed within the layers.

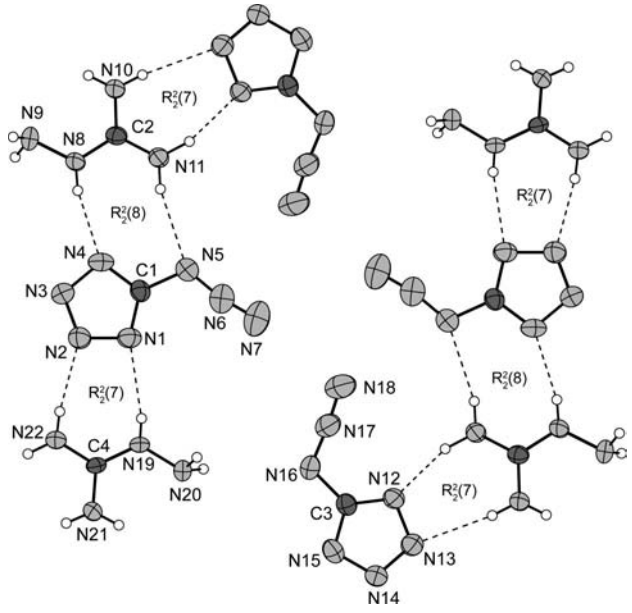

Figure 7. View on the layers in **4**. Thermal ellipsoids represent the 50 % probability level. Selected geometries of the cations: distances (Å): N8−N9 = 1.408(3), N8−C2 = 1.325(3), C2−N10 = 1.323(3), C2−N11 = 1.324(3), N19−N20 = 1.397(3), N19−C4 = 1.315(3), C4−N21 = 1.315(3), C3−N22 = 1.313(3); angles (deg): C2−N8−N9 = 119.2(2), N10−C2−N11 = 120.8(3), N10−C2−N8 = 118.1(2), N11−C2−N8 = 121.1(3).

Guanidinium 5-azidotetrazolate (**5**) semihydrate, which crystallizes in the common monoclinic space group $P2_1/c$, contains two different molecular moieties in the unit cell. The presence of water increases the density to 1.546 g cm^{-3} in comparison to **4**. The structure of the guanidinium cations are in agreement with those of, e.g., guanidinium chloride,[47] perchlorate,[48] or bicarbonate.[49] The C−N distances of the cations are similar to those of **4** and are between 1.30 and 1.33 Å. Again the packing is dominated by a strong hydrogen bond network, resulting in a layer structure along the *b*−*c* plane. A view of the layers is given in Figure 8. Due to the presence of the water, up to 24 different hydrogen bonds can be found. Interestingly only one hydrogen atom of the water participates in the formation of the layers, while the other is directed to another layer at a distance of ca. 3.3 Å.

Lithium 5-azidotetrazolate monohydrate (**6**) crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The density 1.683 g cm^{-3} is in the range found for other lithium tetrazolate salts, e.g., lithium tetrazolate.[50] The lithium cations are coordinated tetrahedrally by the nitrogen atoms N2 and N3 of two different CN_7 anions and two water molecules. As expected, the Li−O distances (∼2.00 Å) are found to be shorter than the Li−N distances (∼2.05 Å). The water molecules bridge the extended molecular moiety (Figure 9) to layers along the *b*−*c* plane (illustrated in Figure 10) by the hydrogen bonds

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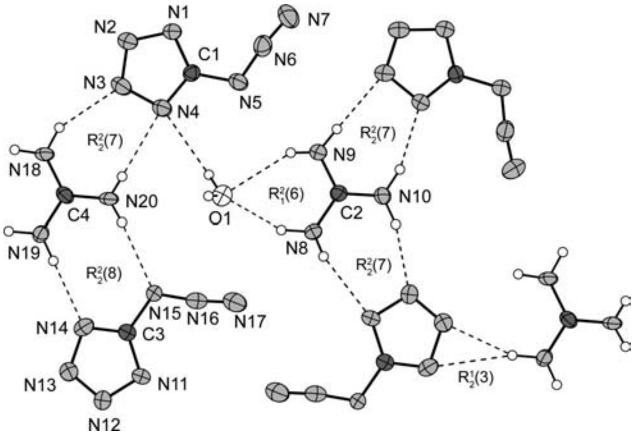

Figure 8. View on the layers of **5** along the a axes. Thermal ellipsoids represent the 50 % probability level. Selected geometries: distances (Å): C2−N8 = 1.330(5), C2−N9 = 1.330(5), C2−N10 = 1.306(5), C4−N18 = 1.318(5), C4−N19 = 1.327(5), C4−N20 = 1.317(5); angles (deg): N8−C2−N9 = 118.5(4), N9−C2−N10 = 120.2(4), N10−C2−N8 = 121.2(4).

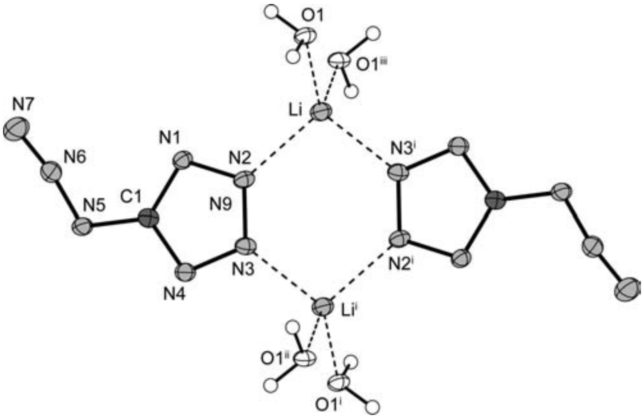

Figure 9. Extended molecular structure of **6**. Selected geometries: distances (Å): Li−N1 = 2.055(3), Li^{i}−N3 = 2.051(3), Li−O1 = 1.996(3); angles (deg): O1−Li−N2 = 117.2(2), O1−Li−O1^{i} = 100.9(1); N2−Li−N3^{i} = 102.32(1); (i) −*x*, 1 − *y*, 2 − *z*; (ii) *x*, 1.5 − *y*, 0.5 + *z*; (iii) −*x*, −0.5 + *y*, 1.5 − *z*.

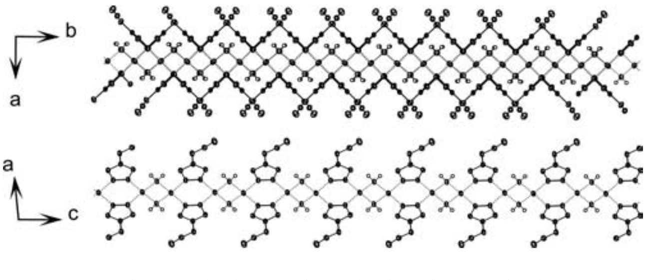

Figure 10. View on the layers along the *b* and *c* axes in the structure of **6**.

O1−H1A···N4 = 0.86(2), 1.94(2), 2.748(2) Å, 156(2)° and O1−H1B···N1 = 0.87(3), 1.96(3), 2.78(2) Å, 157(2)° building a $C_2^2(6)$ graph set.

Sodium 5-azidotetrazoilate (**7**) crystallizes also as a monohydrate in the monoclinic space group $P2_1/c$ with eight molecules in the unit cell and a calculated density of 1.743 g cm^{-3}. The constitution of the CN_7 anion is comparable to those observed for **2**−**6**. In this structure the azide group shows the largest twist out of the ring plane (N1−C1−N5−N6 = −172.6(3)° and N8−C1−N12−N13 = 9.3(4)°). The packing is characterized by the formation of dimeric units (Figure 11), in which the sodium atoms are coordinated nearly octahedrally by two water molecules and four ring nitrogen atoms of different tetrazolates. The azide group does not participate in any coordination to the sodium centers. However, nitrogen atoms N5 and N12 participate in hydrogen bonds (O2−H2A···N5 = 0.83(3), 2.24(3), 2.966(4), 147(3)°; O1−H1A···N12 = 0.84(4), 2.22(4), 2.925(4), 142(4)°). Together with the H-bonds O1−H1B···N8 = 0.72(3), 2.19(3), 2.833(4), 149(4)° and O2−H2B···N1 = 0.84(3), 2.08(3), 2.825(4), 148(3)°, $C_2^2(6)$ chains are formed.

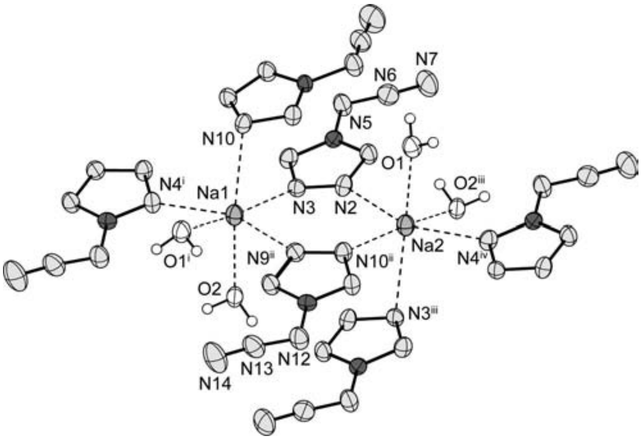

Figure 11. Coordination of the sodium cations in the packing of **7**. Selected coordination geometries: distances (Å): N3−Na1 = 2.499(3), O1−Na1 = 2.429(3), O2−Na1 = 2.348(4), N9−Na1 = 2.568(3), N10−Na1 = 2.711(4), N11−Na1 = 2.511(3); angles (deg): O2−Na1−O1 = 97.7(1), O2−Na1−N3 = 90.56(1), O2−Na1−N11 = 87.3(1), O2−Na1−N9 = 83.88(9), O2−Na1−N10 = 173.97(8); (i) 1 − *x*, −0.5 + *y*, 0.5 − *z*; (ii) 1 − *x*, 0.5 + *y*, 0.5 − *z*; (iii) 1 − *x*, 1 − *y*, −*z*; (iv) *x*, 1 + *y*, *z*.

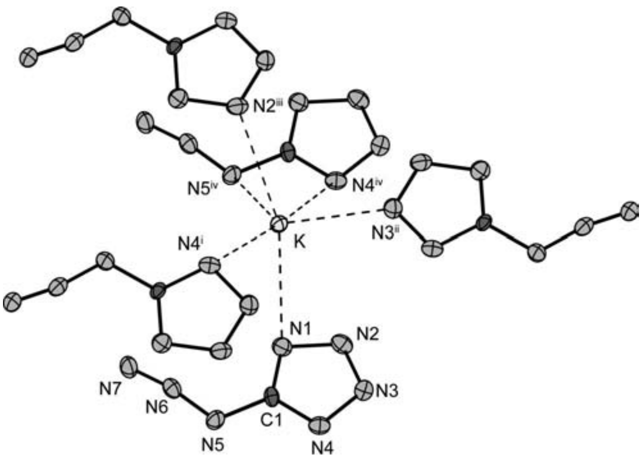

Figure 12. Coordination of the potassium atoms in the structure of **8**. Selected coordination geometries: distances (Å): N1−K = 2.857(2), N2−K = 3.136(2), N2^{iii}−K = 2.849(2), N3^{ii}−K = 2.818(2), N4^{i}−K = 2.878(2), N5^{iv}−K = 3.065(5), N4^{iv}−K = 3.021(2); angles (deg): N1−K1−N4^{i} = 82.78(6), N1−K1−N2^{iii} = 160.24(6), N1−K1−N3^{ii} =100.87(6), N5^{iv}−K1−N4^{iv} = 45.69(6); (i) *x*, 0.5 − *y*, 0.5 + *z*; (ii) 2 − *x*, 0.5 + *y*, 0.5 − *z*; (iii) *x*, 1.5 − *y*, 0.5 + *z*; (iv) *x*, 1 + *y*, *z*.

Potassium 5-azidotetrazolate (**8**) crystallizes in the monoclinic space group $P2_1/c$ with a calculated density of 1.917 g cm^{-3}. The coordination of one potassium cation (Figure 12), which is surrounded by six nitrogen atoms, can be described as distorted octahedral. The coordination distances range from 2.85 to 3.02 Å. This coordination is comparable to that found, e.g.,

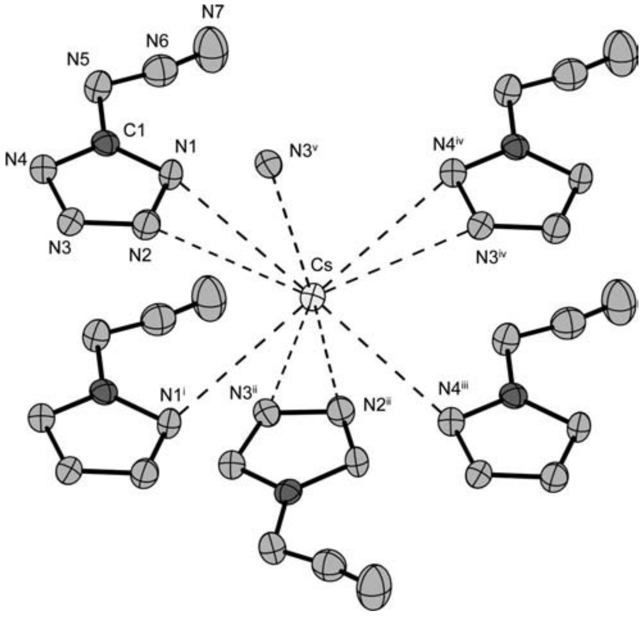

Figure 13. Coordination (<3.5 Å) of the cesium cations in the structure of **9**. Ellipsoids represent the 50 % probability level. Selected geometries: distances (Å): Cs−N2 = 3.153(4), Cs−N1 = 3.357(4), $Cs-N1^i$ = 3.455(4), $N4^i-Cs$ = 3.250(4), $Cs-N3^{ii}$ = 3.181(4), $Cs-N2^{ii}$ = 3.313(4), $Cs-N4^{iii}$ = 3.250(4), $Cs-N3^{iv}$ = 3.242(4), $Cs-N4^{iv}$ = 3.257(4), $Cs-N3^v$ = 3.460(4); (i) 1 + *x*, *y*, *z*; (ii) 2 − *x*, 0.5 + *y*, 0.5 − *z*; (iii) 1 + *x*, 1 + *y*, *z*; (iv) *x*, 1 + *y*, *z*; (v) 1 − *x*, 0.5 + *y*, 0.5 − *z*.

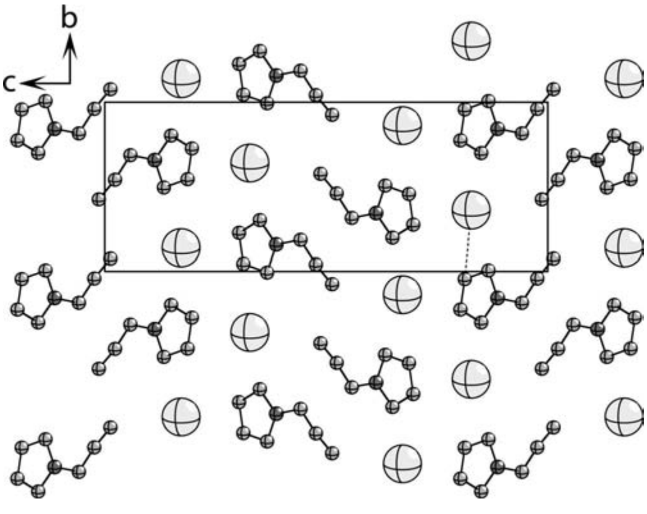

Figure 14. View on the packing of **9** along the *a* axes. Atoms are represented as "ball and sticks". One unit cell is marked.

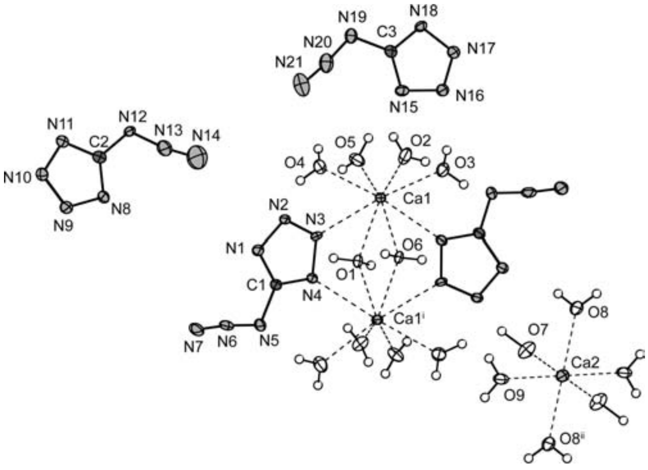

Figure 15. View on the molecular moiety of **10**, whereby two CN_7 anions were removed for better clearness. (i) 1 − *x*, *y*, 0.5 − *z*; (ii) 1.5 − *x*, 0.5 − *y*, 1 − *z*.

in potassium 5-aminotetrazolate[51] or potassium 1-methyl-5-nitriminotetrazolate.[52] It is remarkable that the azide nitrogen atom N5 structure of **8** also participates in the metal coordination sphere.

Cesium 5-azidotetrazolate (**9**) crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell. The density 2.810 g cm^{-3} is the highest observed in this work and is also in the range of other high-nitrogen cesium salts, e.g., cesium tetrazolate.[50] As usual, it is hard to determine an exact coordination number for the cesium cations. The coordination is ninefold (Figure 13) if considering only Cs−N contacts shorter than 3.5 Å. The shortest Cs−N distance is observed for N3. The coordination mode is in agreement with those found in cesium 5-cyanotetrazolate[53] or tetrazolate.[50]

In the packing of **9**, the CN_7 anions are arranged in pillars along the *a* axis (Figure 14). Within the *b*−*c* planes, the shortest Cs−Cs distance is 4.644(1) Å.

The molecular moiety of **10** (Figure 15) is more complex when comparing it with **2**−**9**. The moiety formula is $[Ca(CN_7)_2(H_2O)_{10}][Ca(H_2O)_6](CN_7)_2$. In this structure the two most important coordination modes of Ca^{2+} are included. One calcium atom is surrounded octahedrally by six water atoms in distances of 2.30−2.34 Å, which is also found in hexaquacalcium bis(4-hydroxyazobenzene-3-sulfonate).[54] The other calcium atoms are coordinated eightfold, by six water molecules and the nitrogen atoms N3 and N4 of two different 5-azidotetrazolate anions, while building dimers. A similar coordination mode can be found in the structure of calcium 5,5′-azotetrazolate·16 H_2O.[55] The charge balance in the structure of **10** is formed by four further noncoordinated CN_7 anions.

Spectroscopy. Multinuclear NMR spectroscopy, such as carbon and nitrogen NMR, is a valuable method for characterization of tetrazoles and tetrazolates. The NMR spectra were measured in different solvents (D_6-DMSO, D_2O, and CD_3OD) with respect to TMS (^1H, ^{13}C) and $MeNO_2$ (^{14}N, ^{15}N) as external standards. In the ^{13}C NMR spectra one signal can be observed for the CN_7 anion near 158 ppm (DMSO-d_6) and 160 ppm (D_2O), respectively. In Figure 16 the ^1H, ^{13}C, ^{14}N, ^{15}N, and $^{15}N\{^1H\}$ NMR spectra of **2** in D_6-DMSO are depicted. In the ^1H spectrum a broad signal caused by the hydrazinium protons was observed at 7.07 ppm. The resonance of the ^{13}C carbon atom at 158.1 ppm is shifted to lower field when comparing with **1** (157.5 ppm). In the ^{15}N NMR spectrum six signals could be observed and assigned (δ (ppm): 10.7 (N2/N3), −81.7 (N1/N4), −137.6 (N6), −151.0 (N7), −304.8 (N5) and 332.7 (N6)).

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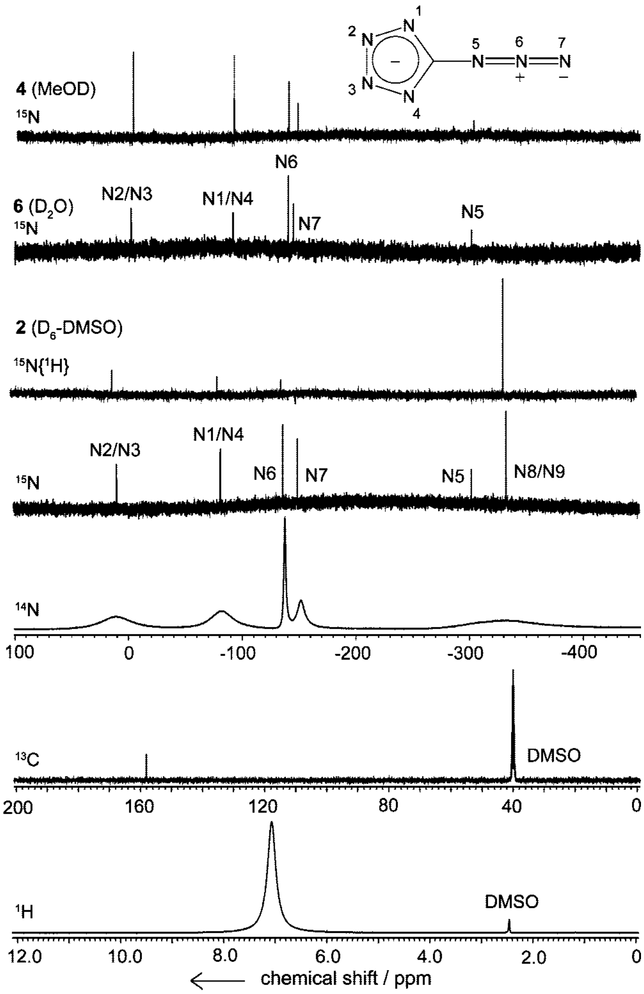

Figure 16. Multinuclear (^{1}H, ^{13}C, ^{14}N, ^{15}N, and ^{15}N{^{1}H}) NMR spectra of **2** and ^{15}N NMR of **4** and **6** in different solvents.

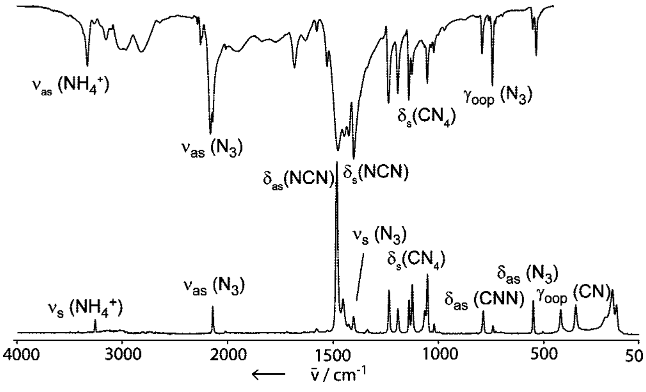

Figure 17. Vibrational spectroscopy of **3** (top: IR, below: Raman).

In the ^{15}N{^{1}H} only the hydrazinium signal is strong in intensity. The ^{14}N spectrum creates broad signals with low resolutions. In addition, Figure 16 illustrates the ^{15}N spectra of **4** (in MeOD) and **6** (in D_2O), whereby the solvent shift can clearly be seen (**4**: δ(ppm): N2/N3 = −2.7, N1/N4 = −92.4, N6 = −141.0, N7 = −149.0, N5 = −305.4); **6**: δ(ppm): N2/N3 = −4.5, N1/N4 = −94.0, N6 = −42.4, N7 = −146.9, N5 = −303.6).

The IR and Raman spectra of **3** are illustrated in Figure 17. The assignments in the figure were done using a frequency analysis from an optimized structure (B3LYP/cc-pVDZ, using the Gaussian 03 software).[56] In addition to some weaker bands due to the ammonia cations, several vibrations of the anions can be detected and assigned. One of the most intense vibrations in the IR spectrum is the ν_{as} vibration of the azide group in the region 2135−2160 cm^{-1} as well as the N−C−N deformation vibrations (δ_s and δ_{as}). In the region 1210−2150 cm^{-1}, also ν_s (N_3) can be detected. The broad signal at ca. 1500 cm^{-1} can be assigned to this symmetric stretching vibration. In the range 980−1100 cm^{-1} many deformation vibrations and combination bands of the tetrazole ring can be found. In the lower frequency regions (ca. 350−550 cm^{-1}) mainly deformation and out-of-lane vibrations are observed.

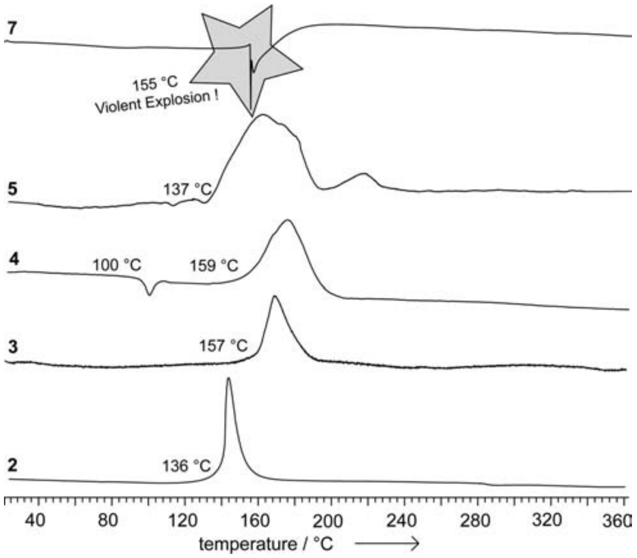

Figure 18. DSC plot of **2**, **3**, **4**, **5**, and **7** (exo up). T_{dec}/°C: **2** = 136 °C, **3** = 157 °C, **4** = 159 °C, **5** = 137 °C, and **6** = 155 °C.

Although there is some similarity to the CN$^-$ anion, the CN_7^- anion should not be described as a pseudohalide (e.g. CN$^-$, N_3^-, OCN$^-$, CNO$^-$, SCN$^-$, and also complexes like $Co(CO)_4^-$). There exist several criteria for pseudohalides which are not met completely by the CN_7^- anion. The CN_7 anion can be protonated yielding the hydrogen acid, and also a poorly soluble silver salt can be formed. However, the synthesis of neutral dimers as well as halogen derivatives cannot be accomplished.

Physicochemical Properties. Since **2**−**10** are highly energetic and explosive compounds and, in particular, (**2**−**5**) have very high nitrogen contents, their energetic behavior was investigated. A detailed description follows.

Thermal Behavior. The thermal behaviors of **2**−**5** and **7** (ca. 1.5 mg) were investigated on a Linseis PT10 DSC[57] (differential scanning calorimeter) at heating rates of 5 °C min^{-1}. (Figure 18) The compounds decompose/explode violently, most of them without melting. Within the nitrogen-rich derivatives **2**−**5** it can be seen from Figure 18 that **2** shows the lowest decomposition temperature of 136 °C. **3** and **4** decompose in the same range (157−159 °C), while a melting point at ca. 100 °C is observed for **4**. Interestingly, **4** shows a broad peak corresponding to decomposition starting at 137 °C. This feature may be due to a loss of the water within the crystal. The sodium salt **7** decomposes at 155 °C. It is not possible to dehydrate **7** either by heating or under reduced pressure. In the measurement of **7** a violent explosion destroyed the setup.

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(56) Gaussian 03; see Supporting Information.

(57) http://www.linseis.com.

Table 3. CBS-4M Results

	p.g.	$-H^{298}$/au	$-G^{298}$/au	NIMAG
CN_7^-	C_s	420.795 948	420.833 397	0
$N_2H_5^+$	C_s	112.030 523	112.058 024	0
NH_4^+	T_d	56.796 608	56.817 694	0
$(H_2N)_2C(NHNH_2)^+$	C_s	260.701 802	260.736 515	0
H		0.500 991	0.514 005	0
C		37.786 156	37.803 062	0
N		54.522 462	54.539 858	0
O		74.991 202	75.008 515	0

Table 4. Literature Values for Atomic $\Delta H°_f{}^{298}$/kcal mol^{-1}

	Ref.[60]	NIST 7[8]
H	52.6	52.1
C	170.2	171.3
N	113.5	113.0
O	60.0	59.6

Table 5. Enthalpies of the Gas-Phase Species M

M	M	$\Delta_f H°$(g,M)/kcal mol^{-1}
CN_7^-	CN_7^-	+114.1
$N_2H_5^+$	$N_2H_5^+$	+185.1
NH_4^+	NH_4^+	+151.9
$(H_2N)_2C(NHNH_2)^+$	AG^+	+161.0

Heats of Formation. Since **2**, **3**, and **4** crystallize without the inclusion of water and carry the highest nitrogen contents, the energetic and thermodynamic properties of **2**−**4** were investigated and are summarized in Table 9. Due to the highly energetic character of **2**−**4**, bomb calorimetric measurements could only be performed with very small amounts and, therefore, the combustion energies are questionable. Thus, an extensive computational study to determine the thermodynamic properties was carried out with the Gaussian G03W (revision B.03) program package.[56] The enthalpies (H) and free energies (G) were calculated using the complete basis set (CBS) method of Petersson and coworkers to obtain very accurate energies. The CBS models use the known asymptotic convergence of pair natural orbital expressions to extrapolate from calculations using a finite basis set to the estimated complete basis set limit. CBS-4 begins with an HF/3-21G(d) geometry optimization; the zero-point energy is computed at the same level. It then uses a large basis set SCF calculation as a base energy and an MP2/6-31+G calculation with a CBS extrapolation to correct the energy through second order. An MP4(SDQ)/6-31+(d,p) calculation is used to approximate higher order contributions. In this study we applied the modified CBS-4M method (**M** referring to the use of minimal population localization) which is a reparametrized version of the original CBS-4 method and also includes some additional empirical corrections.[58,59] The enthalpies of the gas-phase species M were computed according to the atomization energy method (eq 2) (Tables 3−5).[60,61]

$$\Delta_f H°_{(g,M,298)} = H_{(Molecule,298)} - \Delta H°_{(Atoms,298)} + \Delta_f H°_{(Atoms,298)} \quad (1)$$

Table 6. Molecular Volumes

	V_M/Å^3	V_M/pm^3
$[N_2H_5][CN_7]$	151.6[a]	0.152
$[NH_4][CN_7]$	132.3[b]	0.132
$[AG][CN_7]$	201.8[c]	0.202

[a] From X-ray data, V = 264.6 Å^3, Z = 2. [b] V = 606.5 Å^3, Z = 4. [c] V = 807.2 Å^3, Z = 4.

Table 7. Lattice Energies and Lattice Enthalpies

	V_M/nm^3	U_L/kJ mol^{-1}	ΔH_L/kJ mol^{-1}	ΔH_L/kcal mol^{-1}
$[N_2H_5][CN_7]$	0.152	543.4	548.4	131.1
$[NH_4][CN_7]$	0.132	654.6	569.6	136.1
$[AG][CN_7]$	0.202	503.6	508.6	121.6

Table 8. Solid State Enthalpies ($\Delta_f H°$) and Energies of Formation ($\Delta_f U°$)

	$\Delta_f H°$(s) / kcal mol^{-1}	$\Delta_f H°$(s) / kJ mol^{-1}	Δn	$\Delta_f U°$(s) / kcal mol^{-1}	M / g mol^{-1}	$\Delta_f U°$(s) / kJ kg^{-1}
$[N_2H_5][CN_7]$	+168.1	+703.8	−7	+172.2	143.1	+5034.8
$[NH_4][CN_7]$	+129.9	+543.9	−6	+133.5	128.1	+4360.4
$[AG][CN_7]$	+153.5	+642.7	−9	158.8	185.2	+3587.6

The lattice energies (U_L) and lattice enthalpies (ΔH_L) were calculated from the corresponding molecular volumes (Table 6) according to the equations provided by Jenkins et al.[62] and are summarized in Table 7.

With the calculated lattice enthalpies (Table 7) the gas-phase enthalpies of formation (Table 5) were converted into the solid state (standard conditions) enthalpies of formation (Table 8). These molar standard enthalpies of formation (ΔH_m) were used to calculate the molar solid state energies of formation (ΔU_m) according to eqs 2−5.

$$\Delta U_m = \Delta H_m - \Delta nRT \text{ (}\Delta n\text{being the change of moles of gaseous components)} \quad (2)$$

$$C(s) + 2.5\ H_2(g) + 4.5\ N_2 \rightarrow [N_2H_5]^+[CN_7]^-(s)\ (\Delta n = -7) \quad (3)$$

$$C(s) + 2\ H_2(g) + 4\ N_2 \rightarrow [NH_4]^+[CN_7]^-(s)\ (\Delta n = -6) \quad (4)$$

$$2\ C(s) + 3.5\ H_2(g) + 5.5\ N_2 \rightarrow [CN_4H_7]^+[CN_7]^-(s)\ (\Delta n = -7) \quad (5)$$

From Table 8 it can be seen that **2** − **4** are highly endothermic compounds. The enthalpies of energetic materials are governed by the molecular structure of the compounds, and therefore, heterocycles with a higher nitrogen content (e.g. imidazole ($\Delta_f H°_{cryst}$= 14.0 kcal/mol);[63] 1,2,4-triazole ($\Delta_f H°_{cryst}$ = 26.1 kcal/mol); 1,2,3,4-tetrazole ($\Delta_f H°_{cryst}$ = 56.7 kcal/mol))[64] show higher heats of formation. The lower $\Delta_f H°$(s) of **3** in comparison to **4** can be explained by the presence of a further N−N single bond in the structure of **4**, which increases the heat of formation markedly.

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Table 9. Physicochemical Properties of **2**−**4** in Comparison with RDX

	2	**3**	**4**	RDX
formula	$[N_2H_5][CN_7]$	$[NH_4][CN_7]$	$[CH_7N_4][CN_7]$	$C_3H_6N_6O_6$
molecular mass/ g mol^{-1}	143.11	128.12	185.15	222.1
impact sensitivity[a]/J	<1	<1	1	7
friction sensitivity[b]/N	5	5	7	120
ESD[c]/mJ	5	10	40	>150
N[d]/%	88.09	87.48	79.60	37.8
Ω[e]/%	−50.3	−50.0	−64.8	−21.6
T_{dec}[f]/°C	136	157	159	ca. 213
density[g]/g cm^{-3}	1.57	1.61	1.52	1.82
$\Delta_f H_m^{\circ}$[h]/kJ mol	704	540	643	2105
$\Delta_f U^{\circ}$[i]/kJ kg^{-1}	5041	4336	3588	66.5
	calculated values by EXPLO5:			
$-\Delta_E U^{\circ}$[j]/ kJ kg^{-1}	5592	4829	4193	6043
T_E[k]/K	3813	3498	3052	4321
p[l]/kbar	306	287	241	346
D[m]/m s^{-1}	9231	8917	8424	8750

[a] BAM drophammer. [b] BAM methods. [c] Electrical spark sensitivity. [d] Nitrogen content. [e] Oxygen balance. [f] Decomposition temperature from DSC (β = 5 °C). [g] Estimated from X-ray diffraction. [h] Calculated (CBS-4) molar enthalpy of formation. [i] Energy of formation. [j] total energy of detonation, EXPLO5 V5.02. [k] Explosion temperature. [l] Detonation pressure. [m] Detonation velocity.

Detonation Parameters. By using these energies of formation and the densities obtained by X-ray crystallography, several detonation parameters of **2**, **3**, and **4** were calculated using the EXPLO5 computer program.[65,66] This program is based on the steady-state model of equilibrium detonation and uses BKW E.O.S for gaseous detonation products and Cowan−Fickett E.O.S. for solid carbon.[67] The calculation of the equilibrium composition of the detonation products is done by applying a modified White, Johnson, and Dantzig's free energy minimization technique. The program is designed to enable the calculation of detonation parameters at the CJ point. The BKW equation in the following form was used with the BKWN set of parameters (α, β, κ, θ) as stated in the below equations, X_i being the mole fraction of i-th gaseous product, and k_i being the molar covolume of the i-th gaseous product:

$$pV/RT = 1 + xe^{\beta x} \quad x = (\kappa \Sigma X_i k_i)/[V(T + \theta)]^{\alpha}$$

$$\alpha = 0.5, \beta = 0.176, \kappa = 14.71, \theta = 6620$$

Although **2**−**4** are members of the top 15 molecules carrying the highest nitrogen content, they are kinetically stable and show promising decomposition temperatures. The detonation performances of **2**−**4** are summarized in Table 9. The calculated detonation pressure and velocity of **2** exceeds those observed for RDX[68] and also HMX, which is one of the most powerful secondary explosives in use.

More importantly, the specific impulses (I_{sp}) and the molar N_2/CO ratios for the combustion gases are the relevant numbers for the characterization of propellants. Smokeless combustion, which is an inherent feature of high-nitrogen compounds, is not only of environmental interest but also particularly of strategic interest since detection of a gun, missile, or rocket becomes more difficult. Table 10 summarizes the computed isobaric combustion temperatures (T_c, the lower the better for gun propellants), the specific impulses (I_{sp}), and the molar N_2/CO ratios for **2**, **3**, **4**, a 60:40 mixture of **2** with ADN (ammonium dinitramide) and three typical conventional gun propellants (single-, double-, triple-base), and a typical 70:30 solid booster mixture of AP/Al (ammonium perchlorate/aluminum).

Table 10. Computed Propulsion Relevant Parameters (Isobaric Combustion at p = 70 bar)

	density ρ/g cm^{-3}	isobaric comb. temp., T_c/K	specific impulse, I_{sp}/s	molar N_2/CO ratio
NC[a]	1.66	2750	232	0.32
NC[a]/NG (50:50)	1.63	3308	249	0.68
NC[a]/NG[b]/NQ[c] (25:25:50)	1.70	2683	236	1.35
2	1.57	2947	265	96.6
3	1.61	2693	248	96.6
4	1.52	2249	228	93.5
2/ADN[d] (60:40)	1.66	3142	267	6.9
AP/AL (70:30)[e]	2.178	4273	252	–

[a] NC-13.3 (N content 13.3%). [b] NG, nitroglycerine. [c] NQ, nitroguanidine. [d] ADN, ammonium dinitramide. [e] AP/Al, ammonium perchlorate/aluminum.

Whereas single-base propellants are used in all guns ranging from pistols to artillery weapons, the more powerful (see I_{sp}) double-base propellants are commonly used in pistols and mortars. Disadvantages of double-base propellants are the excessive erosion of the gun barrel (see N_2/CO ratio) by the much higher flame temperatures and the presence of a muzzle flash (fuel−air explosion of the combustion products). To reduce erosion and muzzle flash, triple-base propellants with up to 50% nitroguanidine are used in tank guns, large caliber guns, and naval guns. However, the performance of triple-base propellants is lower than that of double-base propellants. Compounds **2**−**4** show relatively low combustion temperatures (comparable to single- and triple-base propellants), with excellent molar N_2/CO ratios (which are usually 0.5 for conventional propellants). The computed specific impulses of **2**, **3**, and even **4** have possible applications as promising energetic components in reduced-erosion gun propellants. Moreover, a 60:40 mixture of **1** with ADN possesses a calculated specific impulse of ca. 15 s higher than that of a mixture of AP/Al commonly used in solid state boosters (space shuttle, Ariane 5).

Sensitivities. For initial safety testing, the impact and friction sensitivities as well as the electrostatic sensitivity were determined.[69] The impact sensitivity (IS) tests were carried out according to STANAG 4489[70] and were modified according to instruction[71] using a BAM (Bundesanstalt für Materialforschung[72]) drophammer.[73] The friction sensitivity (FS) tests were carried out according to STANAG 4487[74] and were modified according to instruction[75] using the BAM friction tester. Appropriate tests could only performed with compounds **2**−**7** and **10**. Compounds **8** and **9** cannot be handled without violent explosions. Compounds **2**−**7** show impact sensitivities smaller than 1 J. Only **10** explodes at a higher value (2 J). However, according to the UN Recommendations on the Transport of Dangerous Goods,[76] compounds **2**−**7** and **10** are classified as "very sensitive" regarding the impact

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sensitivity. The friction sensitivity tests showed the same trends. Except for **4** (7 N), **5** (11 N), and **10** (25 N), all compounds can be initiated by forces smaller than 5 N. However, except for compound **10**, **2**−**9** are classified as extremely sensitive regarding the friction sensitivity. Electrostatic sensitivity tests were performed only for **2**−**5** and were carried out using an small scale electric spark tester ESD 2010EN (OZM Research) operating with the "Winspark 1.15 software package".(77) The electrical spark sensitivities of microcrystalline (1−50 μm particle size) material were determined to be 5 mJ (**2**), 10 mJ (**3**), 40 mJ (**4**), 70 mJ (**5**), 40 mJ (**6**), 20 mJ (**7**), and 160 mJ (**10**). These values are in the range of primary explosives, e.g., lead azide (5 mJ).

Conclusions

From this combined experimental and theoretical work, the following conclusions can be drawn:

(i)The CN_7 anion (5-azidotetrazolate) can be synthesized by deprotonation of 5-azido-1*H*-tetrazole (**1**) using common bases like ammonia, hydrazine, or alkali as well as alkaline earth metal salts.

(ii) 5-Azidotetrazolate salts are extremely sensitive and highly energetic compounds, which should be assigned to the class of primary explosive and only be handled with appropriate precautions. The sensitivities are higher than those of neutral **1** and depend on the hydrogen bond network. Thus the metal salts (K^+, Rb^+, Cs^+) containing no water molecules are highest in sensitivity and explode even in concentrated aqueous solutions.

(iii) The molecular and crystal structures of different salts containing the CN_7 anion were determined for the first time. The geometry of the anion is in agreement with that of **1**.

(iv) Vibrational and NMR spectroscopy are valuable methods to identify CN_7 salts.

(v)An extensive computational study to determine the heat of formation as well as several detonation parameters of the nitrogen-rich compounds hydrazinium (**2**), ammonium (**3**), and aminoguanidinium (**4**) 5-azidotetrazolate was performed. Compounds **2**−**4** are highly endothermic and have good detonation values as well as specific impulses when combusted with suitable oxidizers. However, they are probably too sensitive for practical applications.

(vi) The decomposition temperatures lie in the range 135 to 160 °C.

(vii) The CN_7 anion should not be described as a pseudohalide.

Experimental Section

All reagents and solvents were used as received (Sigma-Aldrich, Fluka, Acros Organics) if not stated otherwise. Melting points were measured with a Linseis PT10 DSC, using heating rates of 5 °C min^{-1}, which were checked with a Büchi Melting Point B-450 apparatus. ^1H and ^{13}C spectra were recorded with a JEOL Eclipse 270, JEOL EX 400 or a JEOL Eclipse 400 instrument. All chemical shifts are quoted in ppm relative to TMS (^1H, ^{13}C). Infrared (IR) spectra were recorded using a Perkin-Elmer Spektrum One FT-IR instrument. Raman spectra were measured using a Perkin-Elmer Spektrum 2000R NIR FT-Raman instrument equipped with a Nd:YAG laser (1064 nm). Elemental analyses were performed with a Netsch STA 429 simultaneous thermal analyzer. Bomb calorimetry was done using a Parr 1356 Bomb calorimeter with a Parr 1108CL oxygen bomb. The sensitivity data were performed using a BAM drophammer and a BAM friction tester. The electrostatic sensitivity tests were carried out using an electric spark tester ESD 2010EN (OZM Research) operating with the "Winspark 1.15 software package".

CAUTION! *5-Azido-1H-tetrazole as well as its salts* **2**−**10** *are partly extremely high energetic compounds with increased sensitivities towards various stimuli, therefore proper protective measures (safety glasses, face shield, leather coat, earthened equipment and shoes, Kevlar gloves and ear plugs) should be used. All compounds should be stored in explosive cases since they can explode spontaneously.*

5-Azido-1*H*-tetrazole (1). **1** was prepared analogously to our recently published procedure:[14a] Cyanogen bromide (530 mg, 5 mmol) was dissolved in a mixture of 15 mL of cold water and 5 mL of MeOH. To this a solution of NaN_3 (650 mg, 10 mmol) in 5 mL of water was added dropwise while cooling in an ice bath. After 2 h, 1 N HCl (5 mL, 0.5 mmol) was added slowly and the solution was allowed to come to room temperature. The mixture was extracted three times with 10 mL of cold diethyl ether. The organic phases were combined, dried with $MgSO_4$, and desiccated.

Hydrazinium 5-Azidotetrazolate (2). 5-Azidotetrazole (**1**) (555 mg, 5 mmol) was dissolved in 20 mL of THF, and 5.5 mL of 1 M hydrazine solution in THF were added slowly. The mixture was warmed to 45 °C, and methanol was added dropwise until a clear solution was obtained. From this, the product crystallized within 3 h and was washed with diethyl ether (458 mg, yield 64 %). Mp: 136 °C (dec.); IR (KBr): $\tilde{\nu}$ = 3363 (s), 3288 (w), 3211 (m), 3072 (m), 2968 (m), 2762 (m), 2641 (m), 2147 (vs), 1625 (w), 1528 (w), 1471 (s), 1403 (m), 1234 (m), 1189 (w), 1134 (m), 1122 (m), 1083 (m), 1053 (m), 1022 (w), 930 (s), 791 (m), 738 (m), 549 (w), 534 w); Raman (1064 nm): $\tilde{\nu}$ = 3363 (4), 3266 (3), 3212 (5), 2139 (19), 1663 (4), 1628 (7), 1604 (5), 1521 (4), 1474 (100), 1403 (13), 1240 (3), 1233 (21), 1189 (10), 1142 (12), 1124 (21), 1082 (11), 1069 (11), 1055 (26), 1023 (3), 931 (9), 790 (10), 739 (6), 552 (18), 413 (9), 345 (23), 237 (10), 196 (9), 157 (12); ^1H NMR (D_6-DMSO): δ (ppm) = 7.07 (N_2H_5); ^{13}C NMR (D_6-DMSO): δ (ppm) = 158.1 (CN_7); ^{15}N NMR (D_6-DMSO): δ (ppm) = 10.7 (N2/N3), −81.7 (N1/N4), −137.6 ($-NN_{\beta}N$), −151.0 ($-NNN_{\gamma}$), −304.9 ($-N_{\alpha}NN$) N5), −332.7 (N_2H_5); *m*/*z* (FAB^-): 110. EA (CH_5N_9, 128.10) calcd: C, 8.39; H, 3.52; N, 88.09 %. Found: not determinable. BAM drophammer: < 1 J; BAM friction test: < 5 N; ESS: 5 mJ.

Ammonium 5-Azidotetrazolate (3). To 5-azidotetrazole (555 mg, 5 mmol) in 10 mL of water, concentrated ammonia solution (2 mL) was added. After stirring for 5 min the solvent was removed at room temperature under reduced pressure, and the raw product was recrystallized from a small amount of ethanol (518 mg, yield 81 %). Mp: 157 °C (dec.); IR (KBr): $\tilde{\nu}$ = 3333 (m), 3156 (m), 3016 (m), 2965 (m), 2814 (m), 2161 (s), 2140 (s), 1681 (m), 1629 (w), 1474 (vs), 1445 (s), 1422 (s), 1399 (vs), 1233 (m), 1190 (m), 1137 (m), 1122 (m), 1050 (m), 789 (w), 740 (m), 548 (w), 532 (m); Raman (1064 nm): $\tilde{\nu}$ = 3490 (7), 3146 (1), 3019 (4), 2802 (3), 2141 (16), 1575 (3), 1482 (100), 1452 (20), 1422 (5), 1402 (10), 1334 (2) 1233 (25), 1191 (15), 1139 (20), 1123 (29), 1052 (35), 1020 (6), 787 (13), 741 (5), 550 (19), 419 (15), 348 (18), 174 (27), 155 (18); ^1H NMR (D_2O): δ (ppm) = 7.08 (NH_4, br); ^{13}C NMR (D_2O): δ (ppm) = 159.8 (CN_7); ^{15}C NMR (D_2O): δ (ppm) = −4.5 (N2/N3), −94.0 (N1/N4), −42.4 (N6), −146.9 (N7), −303.6 (N5). *m*/*z* (FAB^-): 110. EA (CH_4N_8, 128.10) calcd: C, 9.38;

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(72) http://www.bam.de.

(73) http://www.reichel-partner.de/.

(74) NATO standardization agreement (STANAG) on explosive, *friction sensitivity tests*, no. 4487, Ed. 1, Aug. 22, 2002.

(75) WIWEB-Standardarbeitsanweisung 4-5.1.03, Ermittlung der Explosionsgefährlichkeit oder der Reibeempfindlichkeit mit dem Reibeapparat, Nov. 8, 2002.

(76) Impact: Insensitive > 40 J, less sensitive > 35 J, sensitive > 4, very sensitive < 4 J; friction: Insensitive > 360 N, less sensitive = 360 N, sensitive < 360 N a. > 80 N, very sensitive < 80 N, extreme sensitive < 10 N; According to the UN Recommendations on the Transport of Dangerous Goods (+) indicates: not safe for transport.

(77) (a) Zeman, S.; Pelikán, V.; Majzlík, J. *Cent. Eur. J. Energ. Mat.* **2006**, *3*, 45–51. (b) Skinner, D.; Olson, D.; Block-Bolten, A. *Propellants, Explos., Pyrotech.* **1997**, *23*, 34–42. (c) http://www.ozm.cz/testing-instruments/small-scale-electrostatic-discharge-tester.htm.

(78) Linstrom, P. J.; Mallard, W. G. *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, June 2005, National Institute of Standards and Technology, Gaithersburg MD, 20899, http://webbook.nist.gov.

H, 3.15; N, 87.48 %. Found: not determinable. BAM drophammer: < 1 J; BAM friction test: < 5 N; ESS: 50 mJ.

Aminoguanidinium 5-Azidotetrazolate (4). To aminoguanidinium bicarbonate (340 mg, 2.5 mmol) suspended in 5 mL of water, a solution of 5-azidotetrazole (258 mg, 2.5 mmol) in 5 mL of water was added dropwise. The colorless solution obtained was stirred for 15 min at 45 °C until the release of CO_2 stopped and was left for crystallization. After 1 day **4** was obtained as colorless crystals, which were washed with a small amount of cold ethanol and diethyl ether (440 mg, 95 % yield). Mp: 100 °C, 159 °C (dec.); IR (KBr): $\tilde{\nu}$ = 3436 (s), 3316 (s), 3164 (s), 3077 (m), 2247 (w), 2143 (vs), 1671 (vs), 1521 (w), 1467 (s), 1416 (m), 1406 (m), 1231 (m), 1188 (w), 1116 (w), 1054 (w), 1011 (w), 960 (w=, 787 (w), 617 (w), 511 (w); Raman (1064 nm): $\tilde{\nu}$ = 3272 (6), 2146 (22), 1680 (8), 1641 (6), 1559 (9), 1465 (100), 1414 (8), 1235 (29), 1190 (16), 1109 (28), 1056 (29), 963 (37), 789 (14), 741 (6), 622 (8), 551 (21), 543 (19), 517 (20), 418 (29), 335 (26), 161 (31); ^{1}H NMR (MeOD): δ (ppm) = 8.79 (s, 1*H*, N*H*), 7.39 (s, 2*H*, NH_2), 7.10 (s, 2*H*, NH_2), 5.07 (s, 2*H*, NH-NH_2); ^{13}C NMR (MeOD): δ (ppm) = 159.7 (CN_7), 159.2 (AG^+); ^{15}N NMR (MeOD): −2.7 (N2/N3),−92.4 (N1/N4), −141.0 (N6),−149.0 (N7), 287.1 (NH), −305.4 (N5), 312.3 (NH_2), 318.4 (NH_2), 330.8 (NH_2). EA ($C_2H_7N_{11}$, 185.15) calcd: C, 12.97; H, 3.81; N, 83.22 %. Found: C, 12.21; H, 4.32; N 82.69 %; BAM drophammer: < 1 J; BAM friction test: 7 N; ESS: 40 mJ.

Guanidinium 5-Azidotetrazolate Semihydrate (5). The procedure of **5** follows that of **4** using guanidinium bicarbonate (303 mg, 2.5 mmol). **4** was obtained as a colorless crystalline material (421 mg, 94 %). Mp: 110 °C, 137 °C (dec.); IR (KBr): $\tilde{\nu}$ = 3482 (s), 3369 (s), 3123 (s), 2469 (w), 2254 (w), 2144 (vs), 2037 (w), 1650 (vs), 1523 (m), 1469 (s), 1406 (s), 1237 (m), 1191 (m), 1130 (m), 1071 (w), 1049 (m), 791 (w), 741 (m), 669 (m), 632 (m), 553 (w), 534 (w); Raman (1064 nm): $\tilde{\nu}$ = 3363 (4), 3165 (5), 2139 (15), 1644 (15), 1578 (15), 1470 (100), 1405 (22), 1337 (16) 1241 (28), 1194 (24), 1131 (24), 1119 (24), 1051 (39), 1011 (67), 792 (17), 741 (15), 545 (32), 519 (17), 421 (24), 343 (20, 167 (24); ^{1}H NMR (MeOD): δ (ppm) = 5.18 (s, 6*H*, NH_2); ^{13}C NMR (MeOD): δ (ppm) = 159.1 (CN_7), 158.8 (G^+). EA ($C_2H_7N_{10}O_{1/2}$, 179.15) calcd: C, 13.41; H, 3.94; N, 78.19 %. Found: C, 13.13; H, 4.12; N, 77.42 %. BAM drophammer: < 1 J; BAM friction test: 11 N; ESS: 70 mJ.

Lithium 5-Azidotetrazolate Monohydrate (6). 5 mL of aqueous LiOH (96 mg, 4 mmol) solution were added to 5-azidotetrazole (444 mg, 4 mmol) dissolved in 10 mL of MeOH. After stirring for 10 min at 40 °C the solution was filtrated and left for crystallization. After 48 h colorless single crystals were obtained, which were washed with diethyl ether (459 mg, 85 % yield). Mp: 152 °C (dec.). Raman (1064 nm): $\tilde{\nu}$ = 2157 (25), 1479 (100), 1407 (15), 1243 (39), 1205 (12), 1156 (21), 1143 (21), 1068 (46), 792 (11), 746 (7), 553 (26), 429 (16), 353 (22), 167 (27). BAM drophammer: < 1 J; BAM friction test: 11 N; ESS: 70 mJ.

Sodium 5-Azidotetrazolate Monohydrate (7). Cyanogen bromide (530 mg, 5 mmol) was dissolved in a mixture of 15 mL of cold water and 5 mL of MeOH. To this a solution of NaN_3 (650 mg, 10 mmol) in 5 mL of water was added dropwise while cooling in an ice bath. The solution was allowed to come to room temperature and was stirred for 12 h further. Afterwards the solution was extracted two times with 40 mL of EtOAc. The organic phases were combined and abandoned. After 2 days **7** was obtained as colorless needles (453 mg, yield 60 %). Mp: 155 °C (dec.); IR (KBr): $\tilde{\nu}$ = 3602 (m), 3387 (m, br), 3019 (w), 2962 (w), 2855 (w), 2154 (s), 1621 (m), 1466 (s), 1415 (s), 1258 (s), 1231 (vs), 1188 (m), 1153 (m), 1132 (m), 1117 (m), 1071 (s), 1002 (s), 796 (s), 738 (w), 615 (m), 596 (m), 566 (m), 535 (w); Raman (1064 nm): $\tilde{\nu}$ = 3433 (7), 3044 (23), 3017 (23), 2963 (49), 2855 (25), 2145 (18), 1614 (13), 1470 (64), 1413 (18), 1261 (18), 1230 (26), 1201 (15), 1189 (15), 1133 (20), 1119 (21), 1083 (98), 1055 (23), 1001 (16), 811 (100), 739 (12), 620 (27), 596 (21), 573 (39), 550 (26), 439 (40), 422 (33), 346 (26), 273 (18), 165 (27); ^{1}H NMR (D_6-DMSO): δ (ppm) = 4.13 (H_2O br); ^{13}C NMR (D_6-DMSO): δ (ppm) = 158.2 (1C); ^{15}C NMR (D_6-DMSO): δ (ppm) = 8.7 (N2/N3), −83.0 (N1/N4), −138.2 (N6), −151.0 (N7), −304.9 (N5); *m/z* (FAB^-): 110. EA (NaH_2N_7O, 151.06) calcd: C, 7.85; H, 1.33; N, 64.90 %. Found: not determinable; BAM drophammer: < 1 J; BAM friction test: < 5 N; ESS: 20 mJ.

Potassium 5-Azidotetrazolate (8). 5 mL of aqueous LiOH (96 mg, 4 mmol) solution were added to 5-azidotetrazole (444 mg, 4 mmol) dissolved in 10 mL of MeOH. After stirring for 10 min at 40 °C the solution was filtrated and left for crystallization. After 48 h colorless single crystals were obtained, which were washed with diethyl ether (459 mg, 85 % yield). Mp: 148 °C (dec.).

Cesium 5-Azidotetrazolate (9). To 10 mL of an aqueous 5-azidotetrazole (222 mg, 2 mmol) solution, cesium carbonate (326 mg, 1 mmol) was added. After stirring for 10 min at 40 °C the solution was filtrated and left for crystallization in an explosive case. After 48 h three colorless single crystals could be obtained swimming on top of the solution, which were brought to Kel-F oil for X-ray determination. The remaining solution was placed into the explosive case again, where it detonated violently after a few hours.

Calcium 5-Azidotetrazolate Hydrate (10). 5 mL of aqueous LiOH (96 mg, 4 mmol) solution were added to 5-azidotetrazole (444 mg, 4 mmol) dissolved in 10 mL of MeOH. After stirring for 10 min at 40 °C the solution was filtrated and left for crystallization. After 48 h colorless single crystals were obtained, which were washed with diethyl ether (459 mg, 85 % yield). Mp: 173 °C (dec.); IR (KBr): $\tilde{\nu}$ = 3607 (m), 3412 (s), 2256 (w), 2159 (vs), 2152 (s), 1654 (m), 1626 (m), 1543 (m), 1477 (s), 1423 (w), 1403 (m), 1367 (w), 1232 (s), 1210 (m), 1200 (s), 1147 (m), 1077 (w), 1053 (w), 1026 (w), 971 (w), 902 (w), 793 (w), 763 (w), 742 (w), 671 (w), 628 (w), 532 (w); Raman (1064 nm): $\tilde{\nu}$ = 3342 (8), 2143 (37), 1543 (8), 1489 (100), 1463 (67), 1425 (14), 1405 (15), 1247 (23), 1233 (39), 1141 (21), 1075 (23), 1055 (23), 1026 (7), 792 (10), 559 (21), 423 (26), 336 (24), 182 (35); ^{1}H NMR (D_6-DMSO): δ (ppm) = 3.38 (br, H_2O); ^{13}C NMR (D_6-DMSO): δ (ppm) = 158.4 (CN_7); EA ($C_6H_{32}Ca_3N_{42}O_{16}$, 1068.83) calcd: C, 6.74; H, 3.02; N, 55.04 %. Found: C, 6.71; H, 3.81; N, 52.94 %; BAM drophammer: 2 J; BAM friction test: 25 N; ESS: 160 mJ.

Acknowledgment. Financial support of this work by the Ludwig-Maximilian University of Munich (LMU), the Fonds der Chemischen Industrie (FCI), the European Research Office (ERO) of the U.S. Army Research Laboratory (ARL) and ARDEC (Armament Research, Development and Engineering Center) under Contract Nos. N 62558-05-C-0027, R&D 1284-CH-01, R&D 1285-CH-01, 9939-AN-01, W911NF-07-1-0569, W911NF-08-1-0372, and W911NF-08-1-0380 and the Bundeswehr Research Institute for Materials, Explosives, Fuels and Lubricants (WIWEB) under Contract Nos. E/E210/4D004/X5143 and E/E210/7D002/4F088 is gratefully acknowledged. The authors acknowledge collaborations with Dr. M. Krupka (OZM Research, Czech Republic) in the development of new testing and evaluation methods for energetic materials and with Dr. M. Sucesca (Brodarski Institute, Croatia) in the development of new computational codes to predict the detonation parameters of high-nitrogen explosives. We are indebted to and thank Drs. Betsy M. Rice and Edward F. C. Byrd (ARL, Aberdeen, Proving Ground, MD) and Dr. Gary Chen (ARDEC, Picatinny Arsenal, NJ) for many helpful and inspired discussions and support of our work. Last but not least the authors are indebted to and thank Dr. Jan. J. Weigand for many helpful discussions.

Supporting Information Available: (1) X-ray geometry tables, (2) cif files, (3) complete ref 56.[56] This information is available free of charge via the Internet at http://pubs.acs.org/.

JA8077522